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# UK Patent Application GB GB 2 174383 A

(43) Application published 5 Nov 1988

(21) Application No 8510873

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- (22) Date of filing 29 Apr 1985
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- (51) INT CL4 C03C 17/02
- (52) Domestic dessification (Edition H): C1M 474 491 503 WF
- (56) Documents cited None
- (58) Field of search C1M Selected US specifications from IPC sub-class CO3C

### (64) Coloured glass articles

(57) A method for producing a coloured design on toughened glass comprises producing a water-slide transfer of the design in coloured vitreous enamel. The water slide transfer is applied to a glass panel allowed to dry and then passed through a heat treatment cycle in which the glass panel is heated to 640-670°C to fuse the enamels to the glass and rapidly cooled to toughen the glass.

### Coloured glass articl s

5 The present invention relates to a method of making a toughened glass article to which a design in coloured enamels has been applied. The invention is concerned particularly, but not exclusively with a method for producing a stained glass effect on toughened sheet glass such as might be used for glass doors or windows.

Various techniques have been used for producing a coloured effect on glass to simulate stained glass windows. For certain applications it is desirable, if not mandatory, that the glass used should be toughened, it has not however been possible hitherto to provide a design on toughened glass that is durable and simple to apply.

According to the present invention a method for producing a toughened glass article with an applied design in coloured enamels includes applying a water-slide transfer to the glass article, the transfer comprising a design in vitrious coloured enamels, and subjecting the glass panel with the applied design to a glass-toughening heat treatment cycle.

Typically the toughening treatment cycle will 30 involve heating the glass panel to 640°-670°C and rapidly cooling with blasts of cold air in a cycle of about 3 minutes duration.

The transfer design may either be fused to the glass panel in a preliminary heat treatment 35 cycle prior to the toughening cycle or the design may be passed directly to the toughening heat-treatment cycle. When a preliminary heat treatment cycle is used this will typically be for a period of 25 minutes to 1½ hours at a 40 temperature of between 590°-600°C. The duration of the toughening cycle is much shorter and the cooling more rapid than for the preli-

minary cycle.

It might be expected that the rapid heating
and cooling of the toughening cycle would
cause the enamels to frizzle or blister producing an unattractive finish. This might particularly be expected in the process without a
preliminary heat-treatment stage, due to the
effects of the vehicle which carries the enamel
being burnt off. We have found, however,
that coloured designs can be produced without fizzle or blistering provided suitable
enamels are used. By testing commercially
available enamels we have found a range of
colours that can be used to produce satisfactory results.

One particular method of carrying out the invention will now be described by way of 60 example.

A water-slide transfer b aring a multi-coloured design is prepared as follows. The design is printed on the gummed side of a sheet of gummed paper using a screen printing tech-65 nique. The areas of different colours are

printed successively in separate stages using different screens to build up the complete design. To produce a good stained-glass effect transparent vitrious enamels are used for the coloured areas although opaque vitrious enamels may be used for divisions between the colours and for lines of detail.

The colours are made up of lead-bearing glass frits mixed with metallic oxides to give the colour and carried in a printing medium. The glass frits are made from a mixture of lead oxide, boric acid and silica which is fused together and then quenched in water and then dried. The frit is then ground with the metallic soxide to provide the desired colour and mixed with just enough medium to enable it to be printed. The medium is burnt off during the heat treatment and the less medium that has to be burnt off the better the results. The printing medium may be cellulose or resinous and serve to bind the colours together.

After the colours have been printed on the gummed paper, the coloured areas are covered with an acrylic resin cover coat to protect the transfer and hold it together during the transfer process.

When it is desired to apply the transfer to a glass articles such as a float-glass door panel, the transfer is soaked in clean water until 95 loose, lifted from the gummed paper and applied to the flat surface of the glass.

After drying for 4 to 6 hours at room temperature the glass with the applied transfer is passed through a toughening or tempering furnace. The glass enters the furnace and is heated rapidly to a temperature of 640°-670°C. The glass passes back and forth within the furnace until it reaches the desired temperature. During this period all the acrylic 105 resin covercoat and the printing medium are burnt off in the oxidising atmosphere of the furnace. By using as little medium as possible the risk of the burning resin disturbing the surface of the fused enamel and causing frizzle 110 or blistering is minimised. The glass frits and metal oxides melt to form areas of transparent colour that are fused to the surface of the glass panel.

When the glass panel emerges from the furnace it is blasted with cold air to cause rapid cooling of the surface of the glass and consequent toughening of the glass panel. The whole transition through the furnace may be completed in three minutes.

The resulting product is a glass panel which is toughened and has the appearance of stain d glass.

We have found that by choosing suitable enamels satisfactory results can be obtained without frizzle. To ascertain which enamels are suitable, test samples of different commercially-available enamels may be applied to a sheet of glass and then passed through the process of the invention. After firing the resultant areas of coloured glass may be in-

spected. Only the enamels which do not produce frizzle should be used. By using this technique we have found a range of enamels of different colours that can be used. For example, we have found good results using gold oxide based enamel for a ruby colour, cobalt oxide based enamel for a blue colour and chrome or cadmium oxide based enamel for a yellow colour.

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#### CL AIMS

- A method for producing a toughened glass article with an applied design in coloured enamels including applying a water-slide trans-15 fer to the glass article, the transfer comprising a design in vitreous coloured enamels, and subjecting the glass panel with the applied design to a glass-toughening heat treatment cycle.
- 20 2. A method according to claim 1 in which the glass-toughening heat treatment cycle comprises heating the glass article to a temperature of 640°C to 670°C and then cooling the article with blasts of cold air.
- 25 3. A method according to claim 2 in which the glass-toughening heat treatment cycle is completed in 3 minutes.
- A method according to any of the preceding claims in which the glass article is sub-30 jected to a preliminary heat-treatment cycle to fuse the enamels to the glass prior to the toughening cycle.
- A method according to claim 4 in which the preliminary heat-treatment cycle is of 25
   minutes to 90 minutes duration and the article reaches a temperature of approximately 600°C during the preliminary heat-treatment cycle.
- A method according to any of claims 1 to 3 in which the glass article is subjected to 40 the toughening cycle directly after the waterslide transfer has been applied.
- A method according to any of the preceding claims in which the water-slide transfer comprises a sheet of gummed paper on which 45 the design is printed.
  - 8. A method according to any of the preceding claims in which the design is of transparent vitreous enamels.
- A method according to any of the pre-50 ceding claims in which the enamels comprise lead-bearing glass frits mixed with metallic oxides to provide the colours and a printing medium.
- 10. A method according to claim 9 in 55 which the metallic oxides include gold oxide, chrome oxide or cadmium oxide.
  - A method according to claim 9 or 10 in which the printing medium is a cellulose or resinous medium.
- 60 12. A method substantially as hereinbefore described.
  - 13. A toughened glass article produced by the method of any of the preceding claims.

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